Supporting Information: Photocatalytic degradation of organic micropollutant by Zr-MOFs/GO composites

Rina Heu [1,2], Mohamed Ateia [3,*], Dion Awfa [1,4], Patiparn Punyapalakul [5,6] and Chihiro Yoshimura [1]

[1] Department of Civil and Environmental Engineering, Tokyo Institute of Technology, 2-12-1-M1-4 Ookayama, Tokyo 152-8552, Japan; heu.r.aa@m.titech.ac.jp (R.H.); yoshimura.c.aa@m.titech.ac.jp (C.Y.)
[2] Faculty of Hydrology and Water Resources Engineering, Institute of Technology of Cambodia, Phnom Penh 12156, Cambodia
[3] Department of Chemistry, Northwestern University, Evanston, Illinois 60208, USA
[4] Water and Wastewater Engineering Research Group, Institut Teknologi Bandung (ITB), Ganesha 10, Bandung 40132, Indonesia; awfadion@gmail.com
[5] Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand; patiparn.p@chula.ac.th
[6] Center of Excellence on Hazardous Substance Management, Chulalongkorn University, Bangkok, 10330 Thailand
* Correspondence: ateia@northwestern.edu (M.A.)

Table S1: The roles of GO in the enhancement of UiO-66 properties for various applications.

Material	Approach	Purpose	Application	Performance	Ref.
UiO-66_GO	Incorporated nanocomposite components	Increasing the porosity and specific surface area	As adsorbent for CO_2 adsorption	3.37 mmol/g at 298 K and 1 bar	[1]
UiO-66 _GO	Mix matrix membranes (MMMs)	Improving permeability and selectivity	As a filler in MMMs for gas separation	Selectivity of H_2/CH_4 :151 and permeability of H_2 :75 barrer	[2]
UiO-66 _GO	Composite ultrafiltration (UF) membrane	Enhancing of water flux and rejection	As a filler in UF membrane for organic rejection	Permeate flux of BSA: 15 $kg/m^2/h$ and dye rejection: MO (87%) and DR 80 (93.8%)	[3]
UiO-66 _$(COOH)_2$_GO	Hybrid pervaporation membrane	Increasing water flux and separation factor	As a filler for pervaporation membrane	Water flux (EA): 2.42 $kg/m^2/h$ and separation factor (EA): 9751	[4]
UiO-66_NH_2 _GO	Nanocomposite catalyst	Improving photocatalytic performance	Nanocomposite catalyst for organic photosynthesis	Conversion of aromatic alcohols: R-H (18.6%), R-NO_2 (43.1%), R-CH_2 (16.3%), R-F (33%),	[5]
Ce_UiO-66 _GO	Nanocomposite catalyst	Enhancement of photocatalytic performance	Nanocomposite catalyst for reduction of NB and its derivatives	Conversion (80%) and selectivity (98%) of NB	[6]
CdS_UiO-66 _GO	Nanocomposite catalyst	Improving photocatalytic H_2 production activity	Nanocomposite catalyst for generation of H_2 production	H_2 evolution rate: 13.8 mmol/g CdS /h	[7]

Synthesis of Graphene Oxide

First, 1 g of graphite flakes will be added to 50 mL concentrated sulfuric acid (H2SO4) while stirring in an ice-water bath to maintain the temperature under 10 °C. Then, 3 g of potassium permanganate (KMnO4) will be slowly added in the mixture. Then, the suspension will be stirred for 25 mins and sonicate for 5 mins by ultrasonic bath at room temperature. After repeating the stirring-sonication process for 12 times, the suspension will be diluted by 200 mL distilled water, followed by extra 2 h sonication. After sonication, 20 mL of hydrogen peroxide (H2O2) will be added to the exfoliated graphite oxide suspension and stirred until gas evolution ceased to reduce residual permanganate. Then the mixed solute will be washed by 1M hydrochloric acid (HCl) and distill water several times and centrifuged each time for 15 mins at 4500 rpm. Finally, graphene oxide precipitates will be freeze-dried at room temperature and kept dried until use.

Synthesis of UiO-66

First, 1.16 g (5mmol) of zirconium (IV) chloride (ZrCl4) and 0.83 g (5mmol) of terephthalic acid (H2BDC) were dissolved in 150 mL of N,N'- dimethylformamide (DMF). Then, the mixture was placed into a 200 mL Teflon liner within a stainless-steel autoclave and kept reaction in a drying oven at 120 °C for 24 h. After the reaction, the product was cooled down in the room temperature, centrifuged and washed with DMF and methanol repeatedly. Afterward, the washed sample was re-dispersed in methanol for 2 days, centrifuged, and dried in a freeze dryer overnight. Finally, the crystalline UiO-66 was gotten and kept dried until further use.

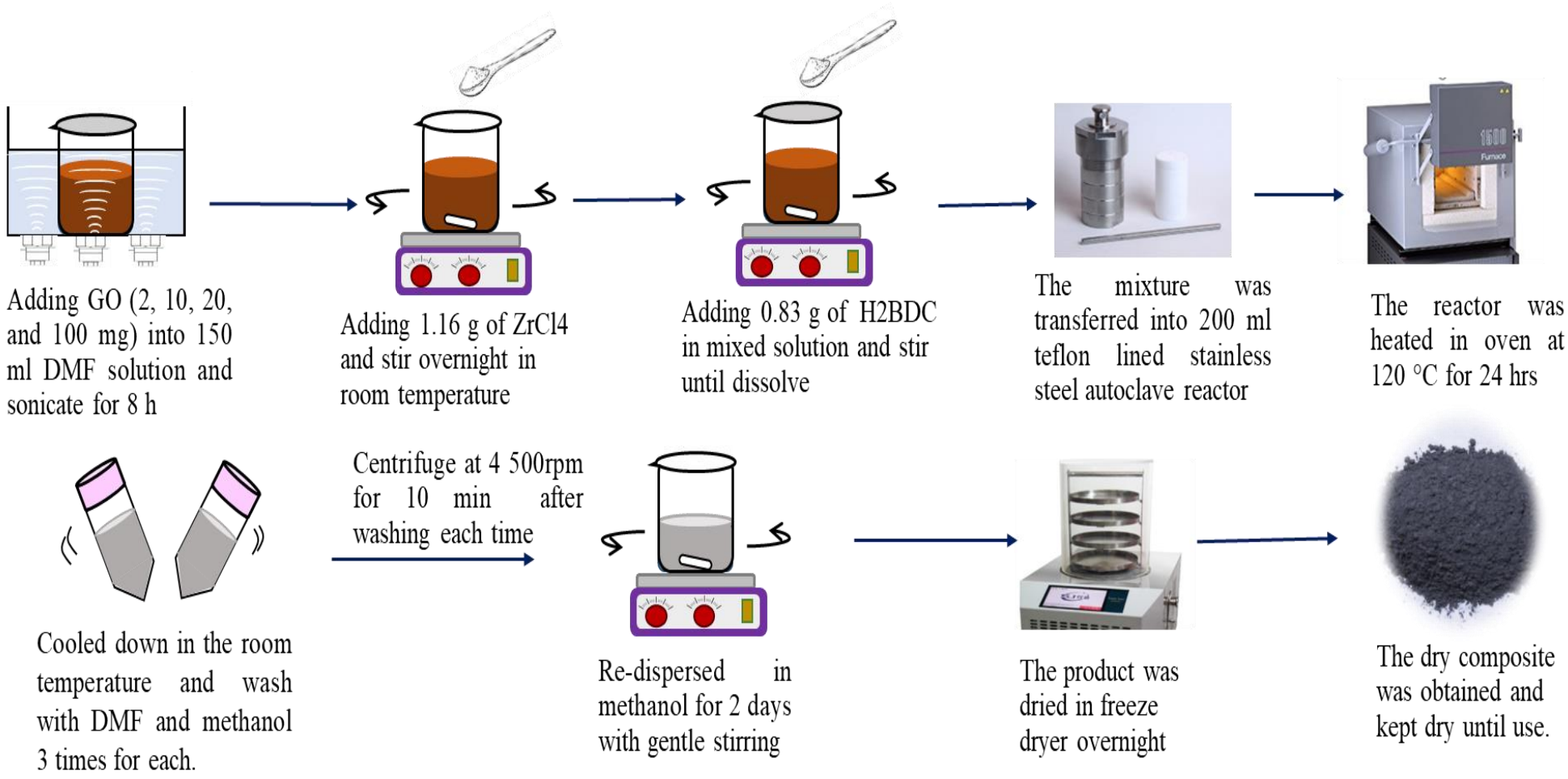

Figure S1. Schematic diagram of synthesis procedures of UiO-66_GO composites.

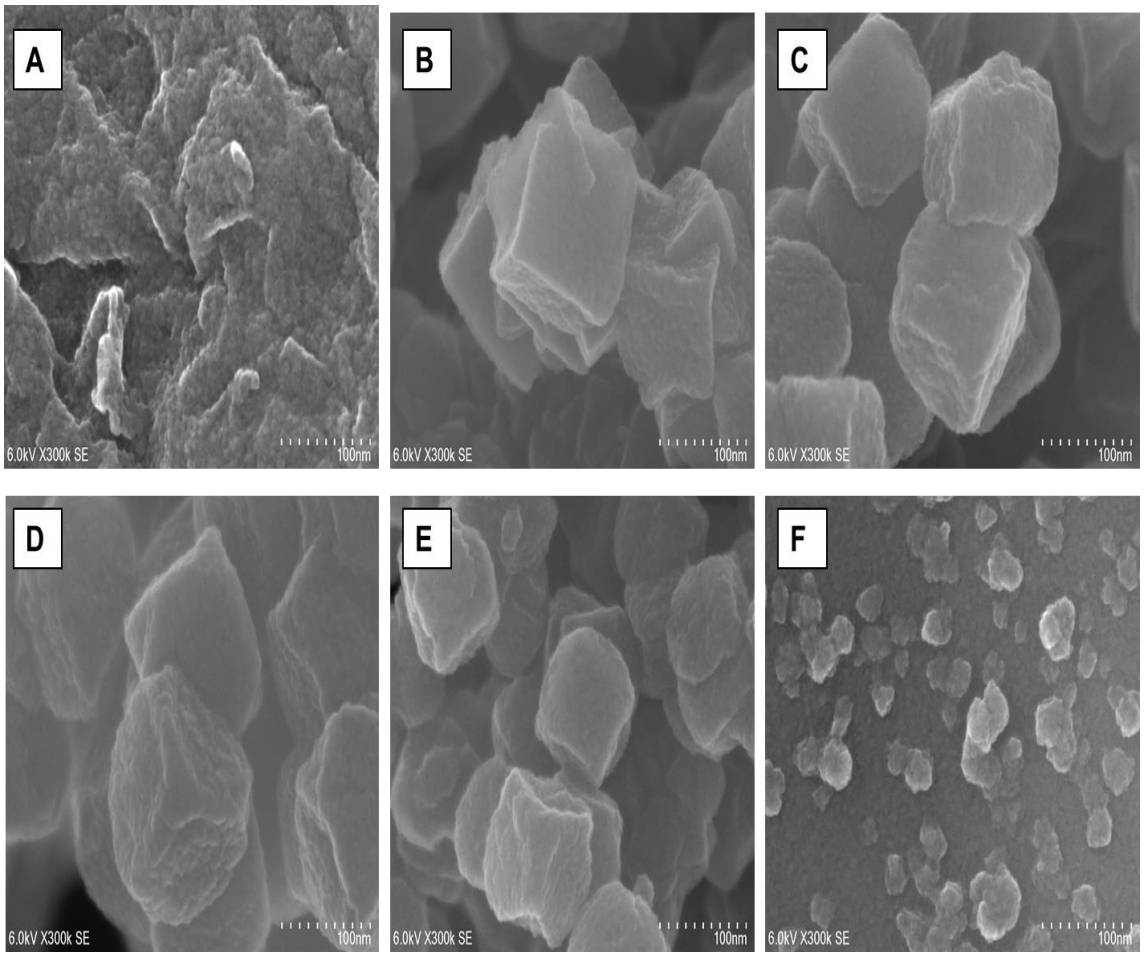

Figure S2. SEM images of [A] GO, [B] UiO-66, [C] UiO-66_GO-0.1%, [D] UiO-66_GO-0.5%, [E] UiO-66_GO-1% and [E] UiO-66_GO-5%.

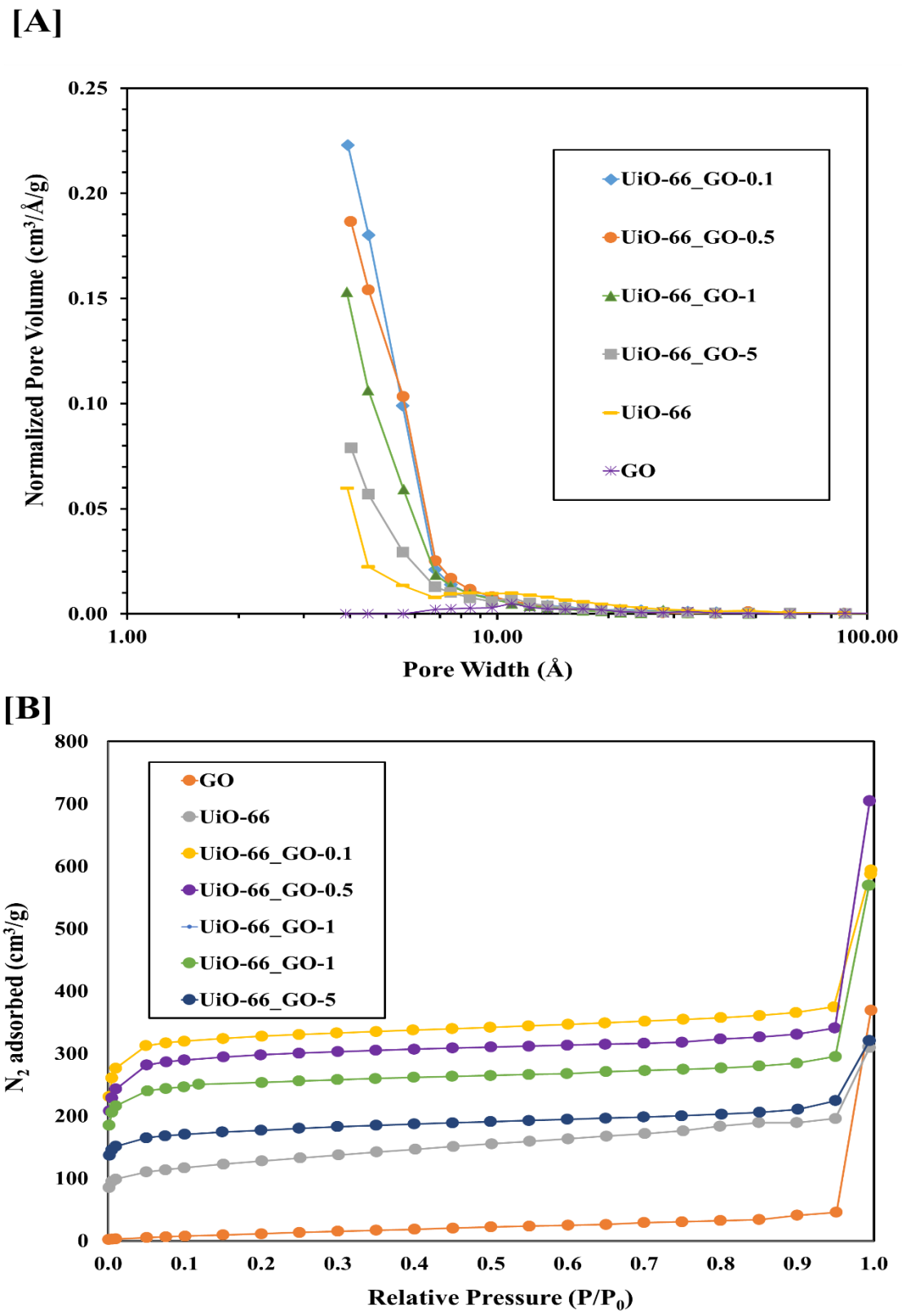

Figure S3. Pore size and pore volume distribution [A] and N_2 adsorption [B] for GO, UiO-66 and composites

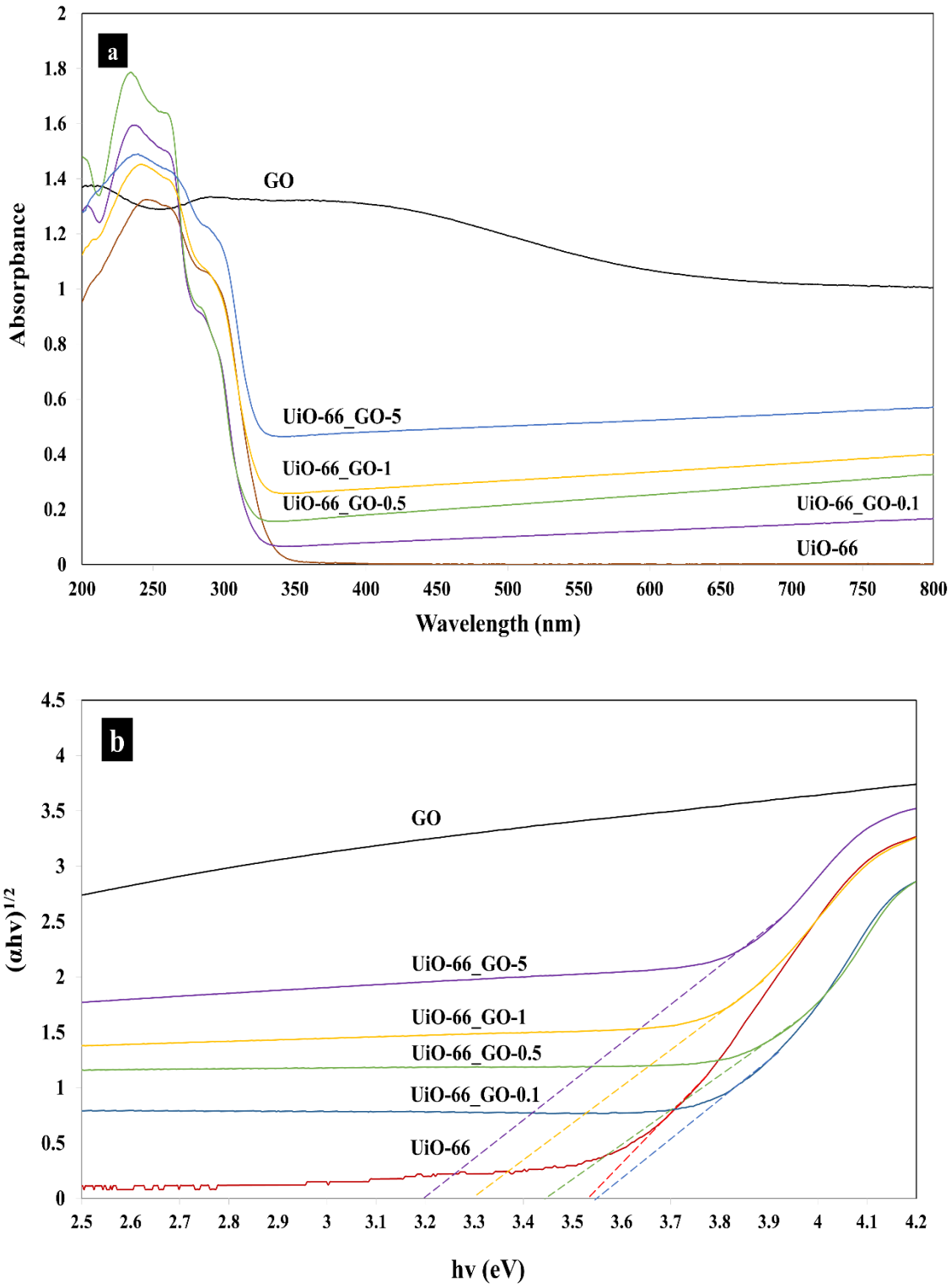

Figure S4. UV-vis absorption spectra (**a**) and (**b**) optical bandgap of GO, UiO-66 and composite.

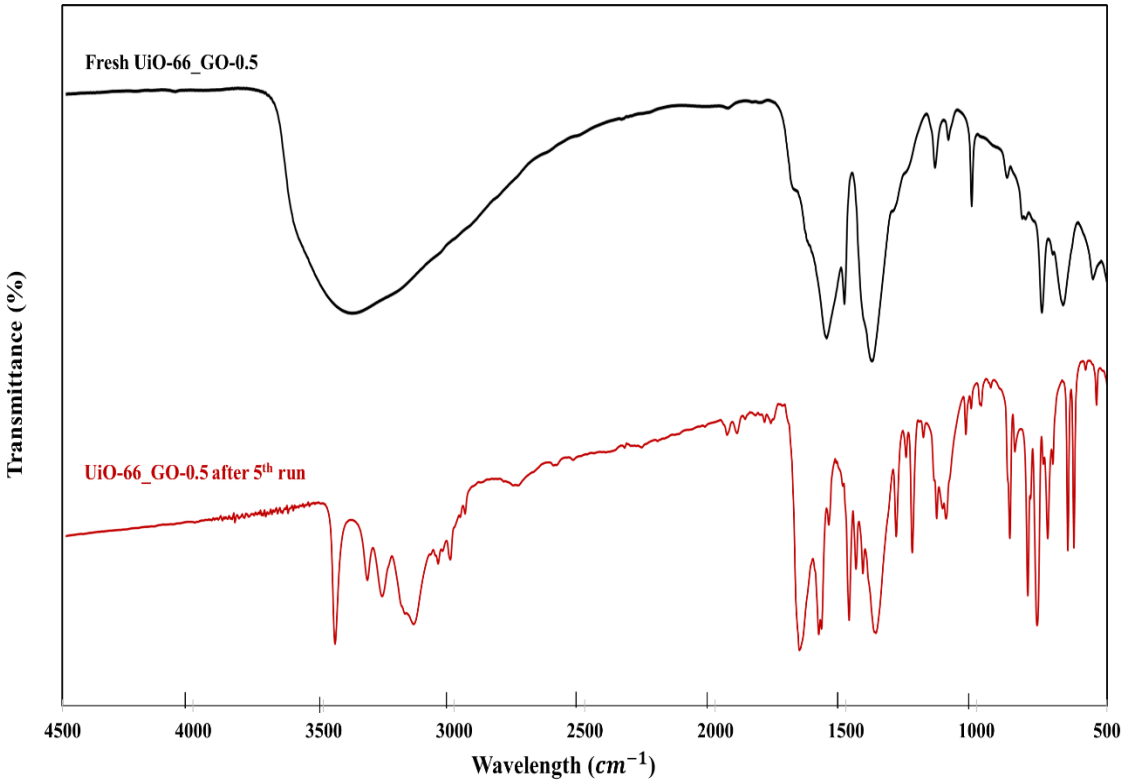

Figure S5. FTIR spectra of fresh UiO-66_GO-0.5 and UiO-66_GO-0.5 after 5th run.

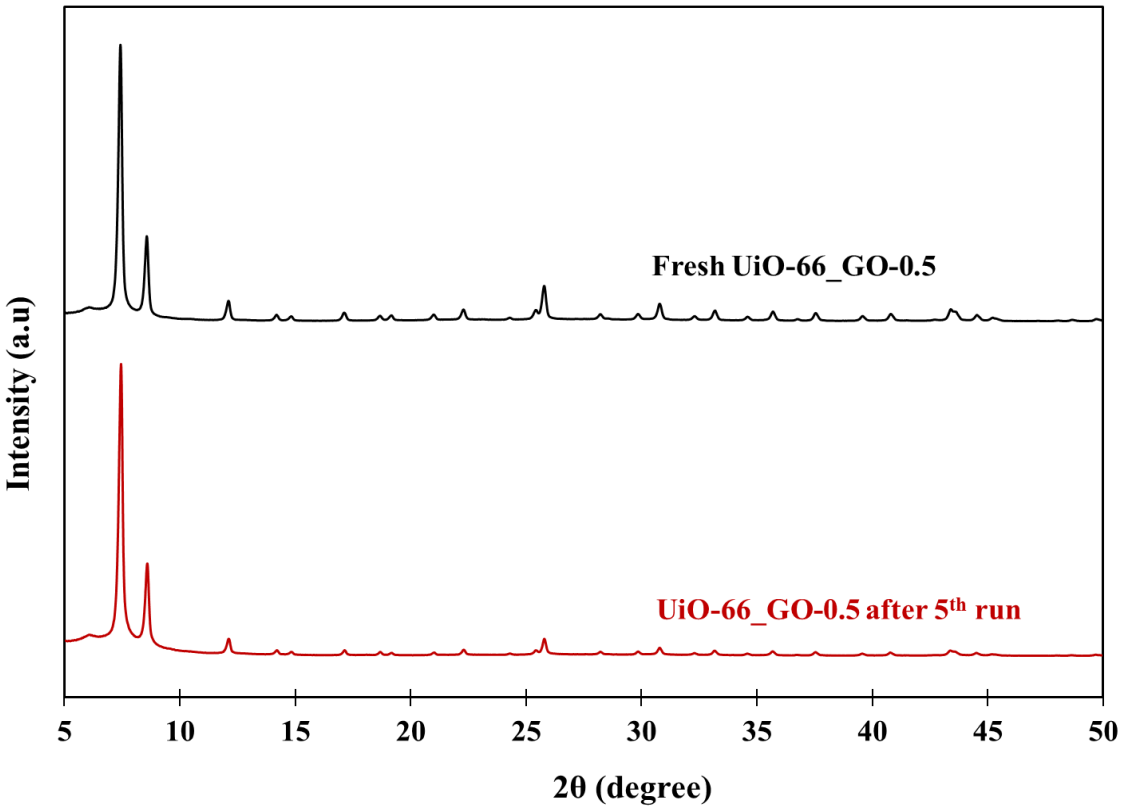

Figure S6. XRD patterns of fresh UiO-66_GO-0.5 and UiO-66_GO-0.5 after 5th run.

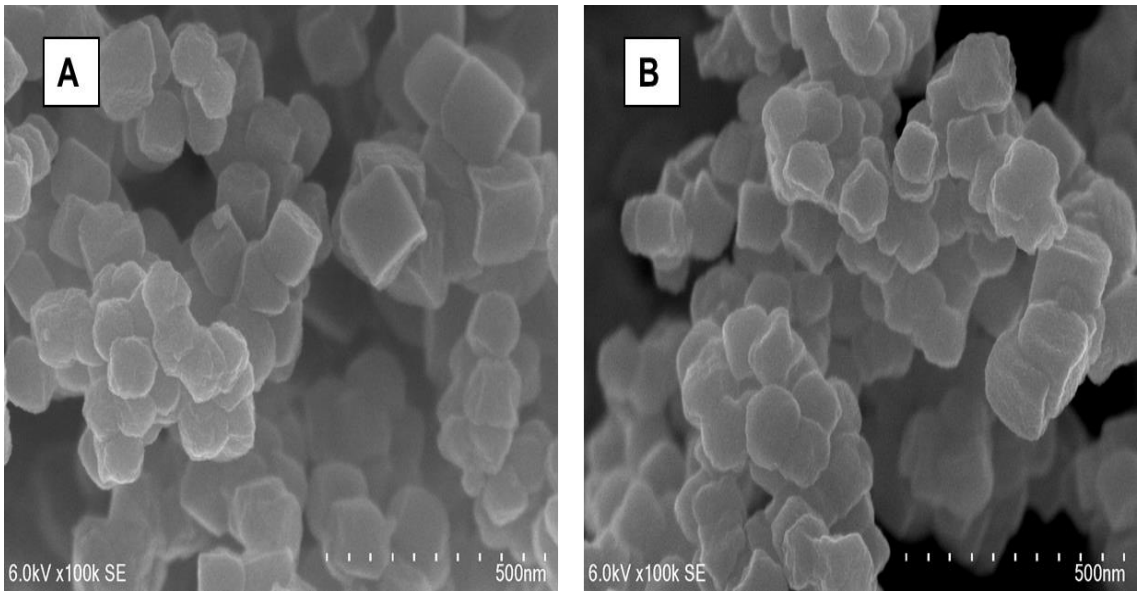

Figure S7. SEM images of [A] fresh UiO-66_GO-0.5 and [B] UiO-66_GO-0.5 after 5th run.

References

1. Cao, Y.; Zhao, Y.; Lv, Z.; Song, F.; Zhong, Q. Preparation and enhanced CO<inf>2</inf> adsorption capacity of UiO-66/graphene oxide composites. *J. Ind. Eng. Chem.* **2015**, *27*, 102–107, doi:10.1016/j.jiec.2014.12.021.
2. Castarlenas, S.; Téllez, C.; Coronas, J. Gas separation with mixed matrix membranes obtained from MOF UiO-66- graphite oxide hybrids. *J. Memb. Sci.* **2017**, *526*, 205–211, doi:10.1016/j.memsci.2016.12.041.
3. Ma, J.; Guo, X.; Ying, Y.; Liu, D.; Zhong, C. Composite ultrafiltration membrane tailored by MOF @ GO with highly improved water purification performance. *Chem. Eng. J.* **2017**, *313*, 890–898, doi:10.1016/j.cej.2016.10.127.
4. Ying, Y.; Liu, D.; Zhang, W.; Huang, H.; Yang, Q.; Zhong, C. High-Flux Graphene Oxide Membranes Intercalated by Metal − Organic Framework with Highly Selective Separation of Aqueous Organic Solution. *ACS Appl. Mater. Interfaces* **2017**, *9*, 1710–1718, doi:10.1021/acsami.6b14371.
5. Xu, J.; He, S.; Zhang, H.; Huang, J.; Lin, H.; Wang, X.; Long, J. Layered metal-organic framework/graphene nanoarchitectures for organic photosynthesis under visible light. *J. Mater. Chem. A* **2015**, *3*, 24261–24271, doi:10.1039/c5ta06838j.
6. Yang, C.; You, X.; Cheng, J.; Zheng, H.; Chen, Y. A novel visible-light-driven In-based MOF/graphene oxide composite photocatalyst with enhanced photocatalytic activity toward the degradation of amoxicillin. *Appl. Catal. B, Environ.* **2017**, *200*, 673–680, doi:10.1016/j.apcatb.2016.07.057.
7. Lin, R.; Shen, L.; Ren, Z.; Wu, W.; Tan, Y.; Fu, H.; Zhang, J.; Wu, L. Enhanced photocatalytic hydrogen production activity via dual modification of MOF and reduced graphene oxide on CdS. *Chem. Commun.* **2014**, *50*, 8533–8535, doi:10.1039/c4cc01776e.